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(19) (CA) **CANADIAN PATENT** (12)

(54) PROCESS AIDS FOR THE CONDITIONING STEP IN THE HOT
WATER EXTRACTION PROCESS FOR TAR SAND

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**"PROCESS AIDS FOR THE CONDITIONING STEP
IN THE HOT WATER EXTRACTION PROCESS FOR TAR SANDS"**

ABSTRACT OF THE DISCLOSURE

5 Anionic surfactants have been found useful as process aids
in the conditioning step and are added to improve recovery efficiency of
the hot water extraction process.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. In the hot water extraction process for recovering bitumen from mined tar sand wherein mined tar sand, hot water, steam and a process aid are introduced into a rotating tumbler and retained and mixed therein for a period of time to produce a conditioned slurry, said slurry being subsequently diluted with additional hot water and then retained under quiescent conditions to cause separation of the slurry components by gravity forces, the improvement comprising:
 - adding an anionic surfactant to the tumbler as the process aid.
2. The process as set forth in claim 1 wherein said anionic surfactant is in the form of a laundry detergent.
3. The process as set forth in claim 1 wherein said anionic surfactant is in the form of a lignosulfonate.
4. The process as set forth in claim 1 wherein said anionic surfactant is in the form of a soap prepared by the saponification of a fatty ester.
5. The process as set forth in claim 1 wherein said anionic surfactant is in the form of a sulfonic acid salt.
6. The process as set forth in claim 1 wherein said anionic surfactant is prepared by sulfonation of a liquid hydrocarbon stream from bitumen upgrading.



BACKGROUND OF THE INVENTION

The invention relates to the hot water extraction process for extracting bitumen from tar sand. More particularly, alternative processing aids are set forth herein that may be used in the tar sand conditioning step of said hot water extraction process to replace some or all of the inorganic alkaline substance heretofore used as a processing aid.

As readily-available supplies of conventional crude oil get used up, the oil industry has turned to tar sand deposits as a source of hydrocarbons. The main tar sand deposit on the North American continent is in the Fort McMurray region of the Province of Alberta in Canada, in an area traversed by the Athabasca River. This deposit is being actively developed at the commercial level.

Tar sand is essentially a mixture of sand grains, water, salts, fine mineral solids of the particle size of clay minerals, and a heavy oil usually referred to as bitumen. It is the bitumen that is of commercial interest. Tar sand also goes by the names of oil sand and bituminous sand. Although the composition varies throughout the deposit, speaking generally, the main constituents analyze at,

20		<u>weight %</u>
	oil	11.59
	water	4.41
	solids	84.00

In theory there are advantages in extracting the bitumen in situ since such processes obviate the need for mining and associated materials handling of huge tonnages of tar sand and tailings, the equipment for which consumes large amounts of capital. In practice, however, mining of tar sand followed by isolating the bitumen therefrom by the hot water extraction process is the preferred commercial method because, in spite of the problems of mining and materials handling, bitumen recovery is very high, normally around 93%.



According to the hot water extraction process as commonly practiced, mined tar sand is added to a conditioning drum, which is horizontally mounted and capable of rotation about its longitudinal axis. This conditioning drum is hereinafter referred to as the tumbler. As well
5 as the tar sand, hot water, steam and, for most tar sand feeds, relatively minor amounts of NaOH are also added to the tumbler. Steam is normally added as two streams, first in relatively large amounts at the front end of the tumbler, and subsequently in the form of trim steam, via sparging valves set in small-bore pipes passing along the length of the inside of
10 the tumbler, to provide more delicate temperature adjustment. The NaOH added assists in the conditioning action, and is used for all tar sand types except the very rich material, that is, for all tar sands of bitumen content less than about 12% bitumen. Commonly, for every 3250 tons of tar sand one adds 610.30 tons of water and such steam as to give a final conditioning
15 temperature in the range of 150° to 180°F, although the process may be operated outside this temperature range.

It is usual for the rate of feed to be set such that it takes less than 10 minutes for tar sand to pass through the tumbler from the inlet to the outlet end. During this time the bitumen is dislodged from
20 the sand particles so that what enters as tar sand, with bitumen and sand tightly bound together (with interstitial water connate to the deposit probably also involved in such bonding), leaves as a mixture, with bitumen, sand, and water merely in loose association, and in such a state that, should suitable conditions be provided, the sand and the bitumen will
25 separate severally from the mixture. This operation in the tumbler is commonly called 'conditioning'. On emerging from the tumbler, the slurry is screened to remove oversized debris, such as rocks and lumps of undigested tar sand, and diluted with further hot water. The diluted slurry then is subjected to the first tar sand components separation step, termed primary
30 separation. This operation is conducted in a primary separation vessel.

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The primary separation vessel contains a bath of hot water maintained in a quiescent condition. The screened, diluted slurry is discharged into the central region of this body of hot water with the following effects:

- 5 Most of the sand, especially the coarse sand, sinks to the bottom and may be pumped out as an aqueous tailings stream;
- The bitumen, in the form of globules, becomes aerated by attachment of air bubbles present in the primary separation
- 10 vessel and, being rendered buoyant thereby, rises to the surface of the vessel where it is collected as a froth (primary froth);
- Bitumen that fails to get aerated, along with much of the fine mineral matter, collectively having a density close
- 15 to that of the aqueous contents of the vessel, has little tendency to either sink or float and so remains in the central region of the vessel.

 The mixture of unaerated bitumen and fine solids (collectively known as "middlings") contains valuable amounts of bitumen that it

20 is advantageous to recover. Hence a portion of the middlings is continuously withdrawn to obtain a further yield of bitumen therefrom. The middlings portion thus withdrawn is advanced to subaerated flotation cells where it is vigorously agitated with air to produce a second froth (secondary froth) and a further tailings stream (secondary tailings).

25 It is advantageous to operate the circuit in such a way as to cause as much of the bitumen as possible to report to the primary froth because the purity of said primary froth is high. Typically, primary froth contains 66.40% by weight of bitumen while secondary froth has only 23.78% bitumen and also contains such large quantities of

30 entrained water and fine minerals that it should be cleaned in a froth settler. After the cleaning step, the secondary froth is combined

with the primary froth and the bitumen is recovered out of the combined froth.

The conditioning of the tar sand that occurs in the tumbler has a marked influence in determining the tendency of the bitumen to join the primary froth. Heretofore, process aids such as sodium hydroxide and sodium silicate, that is, alkaline compounds of monovalent metals, have been added to the tumbler to improve recovery. The present invention is directed toward providing other compounds effective as process aids in the conditioning step of the hot water process for the extraction of bitumen from tar sand.

The mechanism by which inorganic alkaline substances lead to enhanced recovery is not precisely known. It would appear that substances that raise the pH of the tumbler slurry are beneficial. This however fails to go to the heart of the matter, for increased pH is an observed effect arising from the addition of alkaline substances rather than an explanation of their mode of operation.

SUMMARY OF THE INVENTION

It is my observation that recovery may be enhanced by the addition of certain surface active agents to the tumbler slurry without the need for the pH to be increased by alkaline substances. Surface active agents are commonly known as "surfactants" and thus are so referred to hereinafter. Those surfactants that are effective are anionic surfactants. This class of compounds is often taken to consist of synthetic surfactants, that is, compounds where the organic moiety is a hydrophobic organic structure, often, although not exclusively, having one or more sulphonate or carboxylic groups, and the cation is a metal ion with hydrophilic properties. For the purposes of this invention however, anionic surfactants are also taken to include soaps, that is, water-soluble compounds prepared by the saponification of naturally-occurring fatty esters with inorganic basic substances.

The natural pH of an aqueous tar sand slurry normally falls within the range of 7.0 to 8.5. In conventional processing, economical levels of primary recovery with most tar sand types can only be attained when the pH of the tumbler slurry is raised to the range of 9.0 to 9.5 by water-soluble inorganic bases. When anionic surfactants are added to the tumbler in accordance with this invention, they are effective in raising the primary oil recovery to economic levels without the need for added bases.

Broadly stated, the invention is an improvement in the hot water process for extracting bitumen from mined tar sand wherein tar sand is mixed with hot water to form a slurry and retained in a rotating tumbler for a period of time to condition said slurry. The improvement comprises adding an anionic surfactant to the slurry, either before it is introduced into the tumbler or while it is in the tumbler, to improve primary recovery.

DESCRIPTION OF THE PREFERRED EMBODIMENT

A particularly convenient source of anionic surfactants suitable for this purpose is the commercially available laundry detergents, such as those manufactured and marketed by Proctor and Gamble under the trade marks "Tide" and "Drench Extra". In these formulations the anionic surfactant ingredient is usually a combination of modified alkyl sulfate and linear alkane sulfonate. The formulations also contain "fillers" and "builders" which do not play a role in the invention. The invention, however, is not limited to the use of formulations of this type as conditioning aids but may also comprise other anionic surfactants or mixtures of which anionic surfactants form the principal surface active agent. The anionic surfactants may also be used in liquid form.

Synthetic detergents are commonly prepared by sulfonating liquid hydrocarbon and neutralizing the sulfonic acids so obtained with strong inorganic bases, most commonly sodium hydroxide. Considering that the product of a tar sand extraction plant is a liquid hydrocarbon

mixture, a ready feed for the local production of anionic surfactants is available should the scale of operation so warrant. Similarly, much sulfur dioxide is available from the upgrading of bitumen in tar sand processing plants and this may be used for the sulfonating reaction, normally after conversion to sulfuric acid or as fuming sulfuric acid or as sulfur trioxide.

Another readily-available source of anionic surfactants is the lignosulfonates produced in the separation of lignin from wood pulp. Lignin is solubilized by the action of calcium bisulfite and sulfur dioxide to be taken up in aqueous solution as calcium lignosulfonates. In carrying out the tests set forth below, lignosulfonates, sold by Reed Limited under the trade mark "Lignosol", were used.

As is shown in Table I the quantity of surfactant may range from as low as 0.005 to as high as 0.1 wt% expressed as a proportion of tar sand feed. Below 0.005 wt% effectiveness would be expected to be too slight to be of practical value and above 0.1 wt% further increase in quantity of surfactant used would probably raise costs beyond what could be recoverable by the marginal improvement in bitumen recovery that could be expected to result. It is emphasized however, that the range of values here stated is that range used in experimental work, and is given for illustration only. The invention is not thereby restricted to this range but may be operated at such other levels of surfactant addition as may be useful according to the type of tar sand being treated and the costs involved.

Example

The invention is illustrated by the following example.

A number of anionic surfactants have been tested by laboratory-scale extraction runs to determine their efficacy as conditioning aids. The results presented in Table I show how good a primary recovery is achieved without the addition of sodium hydroxide or other inorganic base. In blank runs, that is where no surfactant is added, secondary recovery is enhanced at the expense of primary recovery. By the use of the invention however, primary recovery is improved. The invention

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is seen to be particularly valuable for treating aged tar sand (typified by Tar Sand 2), otherwise difficult to process.

Extraction experiments were performed in a batch extraction apparatus. To a 1.5L stainless steel vessel were added hot water (0.14L) and then tar sand (500g) followed by such additives as are listed in the examples. The vessel was provided with a heated jacket to maintain the contents at the desired temperature (180°F), and with a variable speed agitator. The slurry was agitated at 600 r.p.m. for 10 minutes, 1L of hot water was added, the mixture was stirred for an additional 10 minutes, and then the agitator was stopped and the resulting bituminous froth was skimmed from the surface. The froth from this test had previously been found to be closely analogous to the primary froth of a continuous pilot plant extraction process. The froth was weighed, and analyzed for bitumen content. A yield of secondary froth could be obtained in the batch unit by forcibly adding air to the mixture after the removal of the primary froth.

TABLE I

Surfactant	Surfactant Type	Primary Recovery (%)	Secondary Recovery (%)	Middlings pH
<u>Tar Sand 1</u>				
	None	70.8	24.0	7.9
	Tide* (0.02wt%) Sodium sulfonate	81.7	13.1	8.2
	Tide* (0.06wt%) Sodium sulfonate	89.0	5.5	8.1
25	Na Oleate (0.06wt%) Sodium carboxylate soap	76.0	18.5	8.5
	Na Oleate (0.10wt%) Sodium carboxylate soap	82.7	11.2	8.8

* trade mark

TABLE I (continued)

	Surfactant	Surfactant Type	Primary Recovery (%)	Secondary Recovery (%)	Middlings pH
5	<u>Tar Sand 2</u>				
	None		34.8	52.1	7.5
	Lignosol* HCX (.005wt%)	Lignin sodium sulfonate	49.0	42.9	7.6
10	Lignosol* HCX (0.01wt%)	Lignin sodium sulfonate	58.2	35.0	7.5
	Lignosol* HCX (0.02wt%)	Lignin sodium sulfonate	64.2	28.3	7.5
	Lignosol* HCX (0.05wt%)	Lignin sodium sulfonate	73.9	18.3	7.5
15	Lignosol* AXD (0.01wt%)	Lignin sodium sulfonate	59.0	33.9	7.1
	Lignosol* DXD (0.01wt%)	Lignin sodium sulfonate	60.0	32.7	7.4

Analyses of Tar Sand

20		Bitumen %	Water %	Mineral Solids %	Fines -44 μ %	pH
	Tar Sand 1 (fresh)	11.0	3.9	85.1	10.5	7.8
25	Tar Sand 2	12.0	2.6	85.5	8.6	7.3

* trade mark